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FT-IR Assessment through Pyridine Adsorption of the Surface Acidity of Alkali-Doped MoO_3/TiO_2

C. Martín, I. Martín, C. del Moral, and V. Rives[1]

Departamento de Químicas Inorgánica, Facultad de Farmacia, Universidad de Salamanca, Av. Campo Charro s/n, 37007 Salamanca, Spain

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Adsorption of pyridine on MoO_3/TiO_2 doped with alkali metal cations (Li, Na, K, and Rb) has been studied by FT-IR spectroscopy in order to assess the effect of the nature and concentration of alkali cations on the surface acidity. It has been found that incorporation of the alkali cations leads to a decrease in the surface acidity and of the ratio between the concentration of Brønsted and Lewis surface acid sites. These decreases are due to (i) formation of weak Lewis acid sites (alkali cations) with lower electron affinity than Mo^{6+} and Ti^{4+} and (ii) cancellation of Brønsted sites (Mo–OH) because of formation of alkali molybdates. These effects are more pronounced as the alkali content increases and/or the polarizing character of the alkali cation is increased.

INTRODUCTION

The use of molybdena/titania catalysts for selective oxidation is widespread (1–5). Although several reasons have been advanced to explain the special properties of MoO_3/TiO_2 catalysts compared to those with molybdena supported on other supports (e.g., silica, alumina, magnesia), there is no doubt that surface acidity, among other factors such as the nature of molybdena crystallographic planes that are exposed and the nature of the supported phase or the amount of molybdenum (6–10), plays an important role. Surface acidity can control the way in which the reaction proceeds, e.g., through dehydration, oxygen insertion in the organic molecule, or total oxidation (11–13).

We have previously studied (14–18) the effect of adding different alkali metal cations (Alk) on the physicochemical properties of Alk-metal-doped MoO_3/TiO_2 systems. In order to complete this study, we have now carried out an investigation of surface acidity through FT-IR monitoring of pyridine adsorption. We have also determined the effect of increasing amounts of alkali dopant, as well as of the calcination temperature, since this can also modify the dispersion of molybdena, as a result of melting after calcining at high temperatures.

EXPERIMENTAL

All samples were prepared by impregnation of the support (TiO_2 P25 from Degussa, $S_{BET} \approx 50$ m^2 g^{-1}) with aqueous solutions of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (from Panreac, p.a.). The anatase content was calculated from the intensities of the most intense X-ray diffraction maxima due to anatase and rutile, using the equation given by Criado and Real (19). The amount of molybdenum corresponds to that needed to yield a geometrical monolayer of molybdena (20) on the support (assuming the initial value for the specific surface area of titania), i.e., the amount required to cover completely the exposed surface of the support; this amount corresponds to 5.8% Mo (by weight). The alkali cation had been previously incorporated by impregnation of titania with aqueous solutions of the corresponding nitrate (from Fluka), using a Heidolph VV-60 rotary vacuum evaporator, in order to minimize formation of carbonate species by reaction with atmospheric CO_2. Samples with 1 or 3% (w/w) of alkali metal were prepared. For comparison, another set of samples was also prepared, but without alkali dopant (Alk-free samples). Calcination of these solids was carried out in flowing oxygen (from Sociedad Española de Oxigeno, Spain) for 3 h at 773 K (a temperature high enough to decompose the heptamolybdate to molybdena), although some samples have been calcined at higher temperatures (873 or 1100 K). Chemical analyses of Mo and Alk were carried out by atomic absorption in an ELL-240 apparatus. Samples are designated as M1*XY*/*T*, where X = Li, Na, K, Rb; Y = alkali percentage (1 or 3 wt%); and T = calcination temperature (in K).

The adsorption of pyridine (py, from Fluka) was monitored by FT-IR spectroscopy, using a Perkin-Elmer PC-16 spectrometer, connected to an Ataio 386-SX computer, using special cells with CaF_2 windows. Nominal resolution was 2 cm^{-1}, and 100 runs were averaged to improve the signal-to-noise ratio. Samples were submitted to a conditioning treatment *in situ* which consisted of an outgassing at 670 K for 2 h (residual pressure $\approx 10^{-3}$ N m^{-2}). After equilibration with a small py pressure, the spectrum

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[1] To whom correspondence should be addressed.

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TABLE 1

Summary of the Properties of the Samples

Sample	Mo (%)[a]	Alkali (%)[a]	Anatase (%)[b]	S_{BET} ($m^2 g^{-1}$)
M1/773	5.8	—	52	42
M1/873	5.8	—	50	40
M1/1100	1.2	—	0	10
M1Li1/773	5.8	1	12	19
M1Li3/773	5.8	3	22	20
M1Na1/773	5.8	1	50	39
M1Na1/1100	4.6	1	0	<1
M1Na3/773	5.8	3	51	38
M1Na3/1100	4.6	3	0	<1
M1K1/773	5.8	1	52	44
M1K3/773	5.8	3	52	40
M1Rb1/773	5.8	1	53	47
M1Rb3/773	5.8	3	53	43

[a] % w/w.

[b] % anatase by weight in the support.

was recorded after outgassing at temperatures ranging from room temperature to 673 K. In all cases, the spectrum of the solid was subtracted using the capabilities provided by the computer software. The bands due to adsorbed pyridine were assigned to different modes following the data corresponding to liquid pyridine and protonated pyridine (21, 22).

RESULTS AND DISCUSSION

Results obtained during characterization of the samples are summarized in Table 1 (14–18). In addition to rutile and anatase (the percentage of the latter in the support is given in Table 1), molybdena is detected by XRD in samples M1/773 and M1/873, but not in sample M1/1100, which has a low content of molybdenum because of sublimation as MoO_3 during calcination. Raman spectroscopy provides evidence for the presence of dispersed molybdates in all samples. XRD profiles of the Li-containing samples indicate the presence of Li-molybdate (Li_4MoO_5) and Li-Ti-O species, the latter mainly in samples containing 3% Li. Sodium molybdates, mainly $Na_2Mo_2O_7$, are detected in all samples containing Na (especially for high Na contents); the presence of sodium seems to stabilize molybdenum on the titania surface, Mo losses through sublimation being lower than those in the Na-free sample calcined at 1100 K (see Table 1). Finally, K- and Rb-molybdates ($K_2Mo_4O_{13}$, K_2MoO_4, $Rb_2Mo_4O_{13}$ and Rb_2MoO_4) are also detected in samples containing these cations. Incorporation of Li leads to sintering and rutilization of the support. Total rutilziation is observed in all samples after calcination at 1100 K.

Pyridine and ammonia are two molecules that provide selective information, both qualitative and quantitative, about the surface acidity of metal oxides (23, 24). In the present work we followed the changes in the positions and intensities of the FT-IR bands due to vibrational modes of pyridine when it was adsorbed on our samples. Modes 19*b* and 8*a* were studied, as it has been shown that their positions are very sensitive to adsorption of pyridine on Lewis (Lpy) or Brønsted (Bpy) surface acid sites, due to electron density changes in this molecule through bonding to the surface acid sites. The results are summarized in Table 2.

Alkali-Free Samples

The spectra recorded after adsorption of pyridine on the alkali-free supports are very similar (see Fig. 1A). Bands are recorded always in the same positions, although with different relative intensities. Hence, the strength and nature of the surface acidic sites should be almost the same in all cases. As shown in Table 2, bands recorded at 1610 ± 2 and 1488 cm^{-1} are ascribed to modes ν_{8a} and ν_{19b} of corodinated pyridine, and those at 1640 ± 1 and 1538 cm^{-1} to modes ν_{8a} and ν_{19b} of pyridinium ion. As these bands are recorded in all cases, both Brønsted and Lewis surface acid sites should exist in all samples. The band due to mode ν_{8a} of coordinated pyridine is recorded

TABLE 2

FT-IR Absorption Bands (cm^{-1}) for Normal Modes of Pyridine, Recorded upon Adsorption at Room Temperature on the Samples Studied and Outgassing at Room Temperature[a]

Sample	Bpy		Lpy		Bpy/Lpy
	8a	*19b*	*8a*	*19b*	
M1/773	1638	1538	1613	1448	2.0
M1/873	1640	1537	1610	1449	1.4
M1/1100	1641	1538	1608	1448	0.7
M1Li1/773	—	—	1598	1443	0
M1Li3/773	—	—	1596	1441	0
M1Na1/773	1640	1537	1609 1592	*1449* 1442	0.1
M1Na1/1100	1639	1538	1608 1593	*1448* 1442	0.9
M1Na3/773	—	—	1593	1442	0
M1Na3/1100	—	—	1593	1442	0
M1K1/773	1640	1536	1607 1588	*1448* 1440	0.1
M1K3/773	—	—	1606 1588	1440	0
M1Rb1/773	1639	1538	1607 1586	1446 1439	0.2
M1Rb3/773	—	—	1605 1586	*1447* 1440	0

[a] Italicized figures correspond to shoulders.

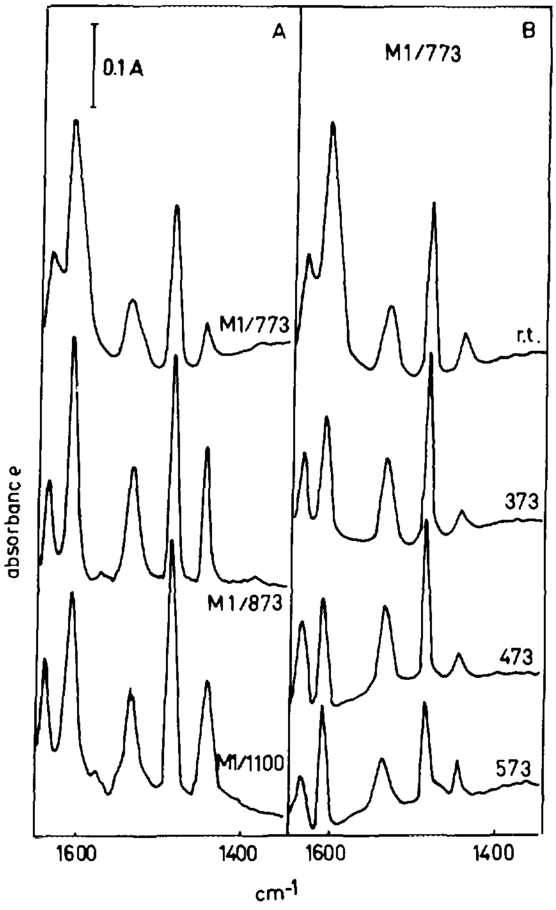

FIG. 1. (A) FT-IR spectra recorded after adsorption of pyridine at room temperature on alkali-free molybdena/titania samples M1/773, M1/873, and M1/1100 and outgassing at the same temperature. (B) FT-IR spectra recorded after adsorption of pyridine at room temperature on sample M1/773 and outgassing at the indicated temperatures (r.t., room temperature).

at higher wavenumbers than that for the original TiO_2 (1603 cm^{-1}) (25, 26), suggesting that pyridine is not coordinated to Ti^{4+} but to Mo^{6+} species. Development of bands due to pyridinium, after incorporation of Mo^{6+}, indicates that surface acid Brønsted sites are associated with molybdate species (Mo^{6+}–OH).

Spectra recorded upon outgassing sample M1/773, previously exposed at room temperature to py vapour, at increasing temperatures are included in Fig. 1B. As the outgassing temperature increases, all Lpy bands shift slightly toward larger wavenumbers. In addition, the intensities of all bands decrease, and the bands finally vanish after outgassing at 673 K, indicating that pyridine molecules are strongly held to surface Lewis sites (Mo^{6+}) and Brønsted sites (Mo–OH).

According to these data, some differences in the acidity of the samples can be envisaged as the calcination temperature is increased (samples M1/773, M1/873, and M1/1100). In order to quantify these differences, the areas of the bands due to the ν_{19b} mode of Bpy and Lpy sites at 1538 and 1450 cm^{-1} have been measured, together with their ratio (Bpy/Lpy; see Table 2). Changes in these values have been plotted in Fig. 2 vs the calcination temperature. A sharp decrease in this ratio is observed as the calcination temperature is increased. This decrease can be related to the decrease shown in Table 1 for the specific surface area of the samples as the calcination temperature is increased (873 or even 1100 K) and/or to surface dehydroxylation (Brønsted sites are associated with Mo^{6+}–OH moieties). However, it can be initially assumed that a specific surface area decrease through sintering would affect the surface concentration of both Brønsted sites *and* Lewis sites, and so the Bpy/Lpy ratio should not necessarily decrease as the specific surface area decreases. The sample calcined at 1100 K has a Mo loading lower than that calcined at 773 K, because of MoO_3 removal through sublimation (80% of the initial Mo content). The Bpy/Lpy ratio (0.7) in this sample calcined at 1100 K is larger than that found in a previous work for a MoO_3/TiO_2 sample containing the same amount of molybdenum (1.2%), but calcined only at 773 K (27), where MoO_3 sublimation has not taken place. A plausible explanation for this behavior would be that calcination at such a high temperature, high enough to melt molybdena, leads (in addition to MoO_3 removal through sublimation and in addition to rutilization and sintering) to redispersion of molybdena on the surface support as two-dimensional

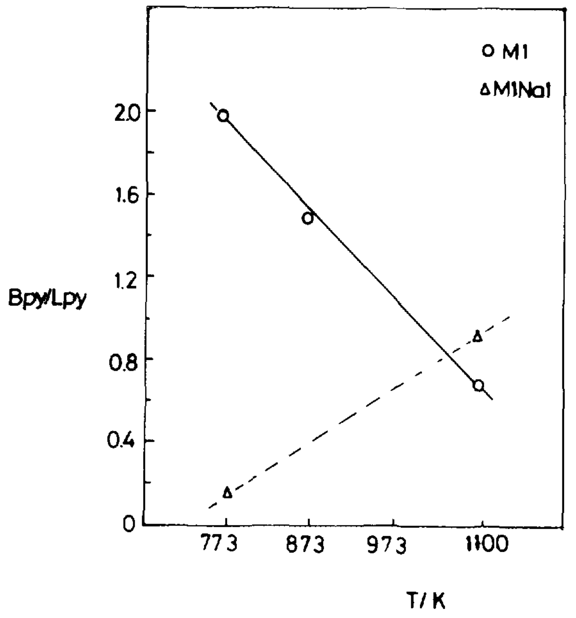

FIG. 2. Bpy/Lpy ratio vs calcination temperature for the alkali-free and Na-containing molybdena/titania samples.

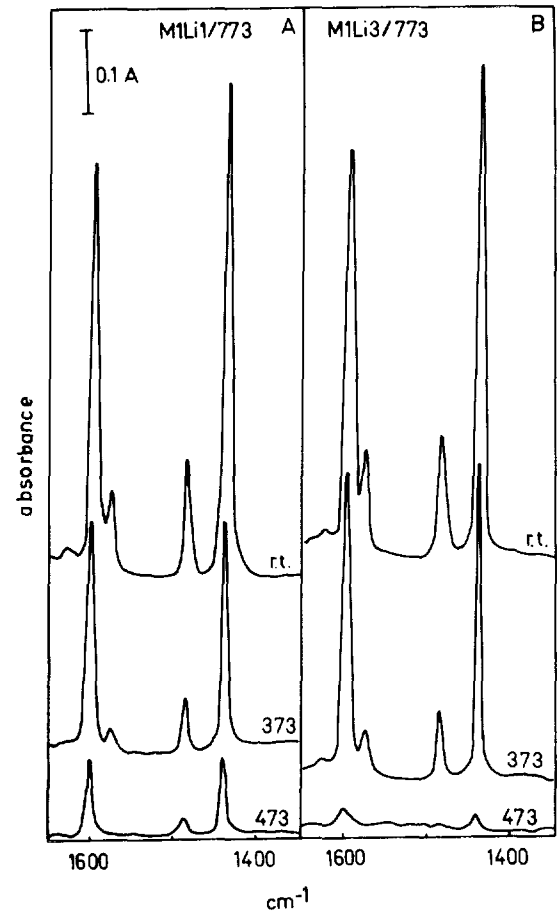

FIG. 3. FT-IR spectra recorded after adsorption of py at room temperature on the Li-containing samples and outgassing at the indicated temperatures.

molybdenum oxide species, whose Brønsted acidity is higher than that of bulk (three-dimensional) molybdena (28). This conclusion is confirmed by the results obtained with the Na-doped samples (see below).

Lithium-Doped Samples

The spectra recorded upon adsorption at room temperature of py on the Li-containing samples and outgassing at increasing temperatures are given in Fig. 3. The bands recorded upon outgassing at room temperature, included in Table 2, correspond to coordinated pyridine only; the absence of bands due to pyridinium ion indicates the lack of Brønsted sites.

Upon outgassing at increasing temperatures, the intensities of the bands decrease faster than those for the Alk-free samples (i.e., the bands are weaker even for the same outgassing temperature), and no band is recorded after outgassing at 573 K. On the other hand, bands are recorded in all cases at wavenumbers lower than those for the Alk-free samples. These two facts (lower wavenumbers and ease of removal) suggest that py molecules are weakly held on the solid surface, probably simply physisorbed or hydrogen-bonded (29). However, in such a case no band would have been recorded upon outgassing at temperatures around 473 K. Thus, as medium intensity bands are recorded (especially in the case of sample M1Li1) upon outgassing at this temperature and no change is observed in the ν_{OH} region, we conclude that py is adsorbed on Lewis sites, probably coordinatively unsaturated Li^+ cations present on the sample surface, as previously reported (15, 26) for alkali-doped titania.

Although the differences between samples M1Li3/773 and M1L1/773 are not too evident, it is noticeable that the bands are more easily removed for the first of these samples, as can be easily concluded from the spectra recorded upon outgassing at 473 K (Figs. 3A and 3B).

Sodium-Doped Samples

The spectra recorded upon adsorption of py and outgassing at room temperature are presented in Fig. 4, and the values corresponding to the positions of the bands are summarized in Table 2.

For low sodium contents (samples M1Na1/773 and M1Na1/1100) the bands recorded are due to coordinated and protonated py. Bands due to modes ν_{8a} and ν_{19b} of pyridine adsorbed on Lewis sites are split for both samples. This splitting indicates the presence of two types of Lewis sites on the surface of this solid, the stronger one (responsible for the bands at 1608 and 1448 cm^{-1}) associated with coordinatively unsaturated Mo^{6+} species, and the weaker one (responsible for the bands at 1593 and 1442 cm^{-1}) with coordinatively unsaturated Na^+ species, similar to those observed for the Li-doped samples, although in this case only the weak sites were detected (see above). The intensities of all bands decrease as the outgassing temperature increases; those recorded at lower wavenumbers (due to weak surface Lewis acid sites) are removed by outgassing at 473 K.

The Bpy/Lpy ratio (Table 2 and Fig. 2), calculated as above, is larger for samples calcined at 1100 K (0.9) than for samples calcined at 773 K (0.1); the sharp specific surface area decrease would account for a decrease in both the Brønsted and the Lewis sites. As Brønsted sites are associated with Mo–OH groups, a lower Bpy/Lpy ratio would be expected for sample M1Na1/1100 because of MoO_3 removal upon calcination at very high temperature. The results observed, however, are probably due to the same reasons as given above for the alkali-free samples, in the sense that calcination above the melting point of molybdena increases the surface Brønsted acidity because of a better dispersion of the Mo-containing species; this process is even more marked in the present case, as

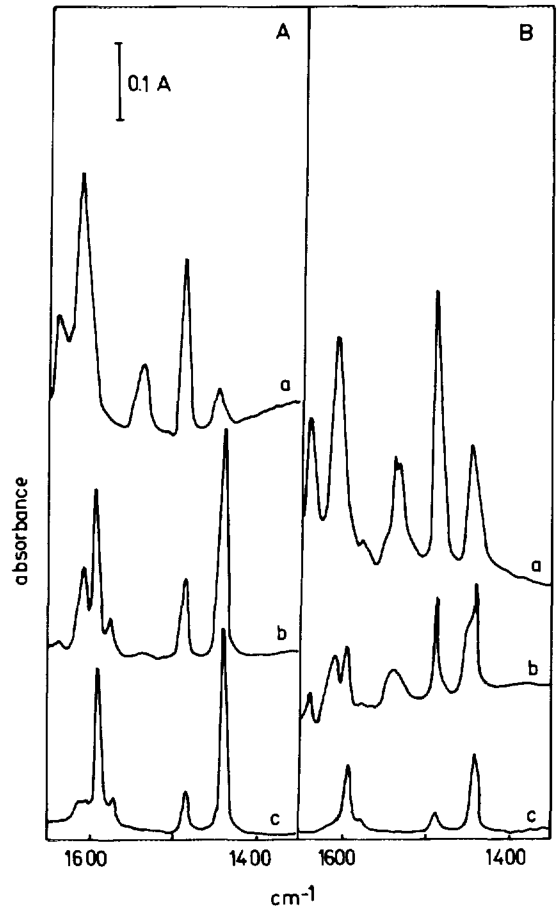

FIG. 4. FT-IR spectra recorded after adsorption and outgassing of py at room temperature on samples (A) a, M1/773; b, M1Na1/773; c, M1Na3/773. (B) a, M1/1100; b, M1Na1/1100; c, M1Na3/1100.

the simultaneous presence of sodium and molybdenum stabilizes the latter on the titania surface, thus avoiding MoO_3 sublimation (see the chemical analysis results in Table 1).

Spectra for the Na-rich samples (Fig. 4) are rather similar to those recorded for the Li-containing samples; only bands due to pyridine adsorbed on weak Lewis acid sites (coordinatively unsaturated Na^+ cations) are recorded (Table 2). The Lewis acid sites existing in these samples are weaker than those in samples with low Na content, as the bands are removed upon outgassing at lower temperatures (ca. 373 K).

Potassium-Doped Samples

The spectra recorded upon adsorption of pyridine on these samples are shown in Fig. 5. Bands due to coordinated py and to the pyridinium cation are recorded for sample M1K1/773, but for sample M1K3/773 the bands are due only to coordinated py (Table 2); i.e., no Brønsted sites exist. As observed with the Na-containing samples, the bands due to ν_{19b} and ν_{8a} modes of Lpy sites split, with two components at 1448 and 1440 cm^{-1} and 1607 and 1588 cm^{-1}, respectively, suggesting two types of surface Lewis acid sites: the weak ones again correspond to K^+ species (responsible for bands at lower wavenumbers and which are removed upon outgassing even at 473 K), and the stronger ones are associated with Mo^{6+} species and are responsible for the bands at 1448 and 1607 cm^{-1}. The Bpy/Lpy ratio is only 0.1 (Table 2), very much lower than the value found for the Alk-free samples.

Only the weak acid Lewis sites (associated with K^+ species) are detected for sample M1K3/773, as the band due to mode ν_{19b} of coordinated py does not split. Upon outgassing at increasing temperatures a decrease in the intensities of the bands is found (see Fig. 5). The bands vanish at a lower temperature for the higher Alk-loaded sample, indicating a weaker strength of the acid sites.

Rubidium-Doped Samples

The pyridine spectra on sample M1Rb1 (Fig. 6A) are very similar to those described above (Table 2) and are

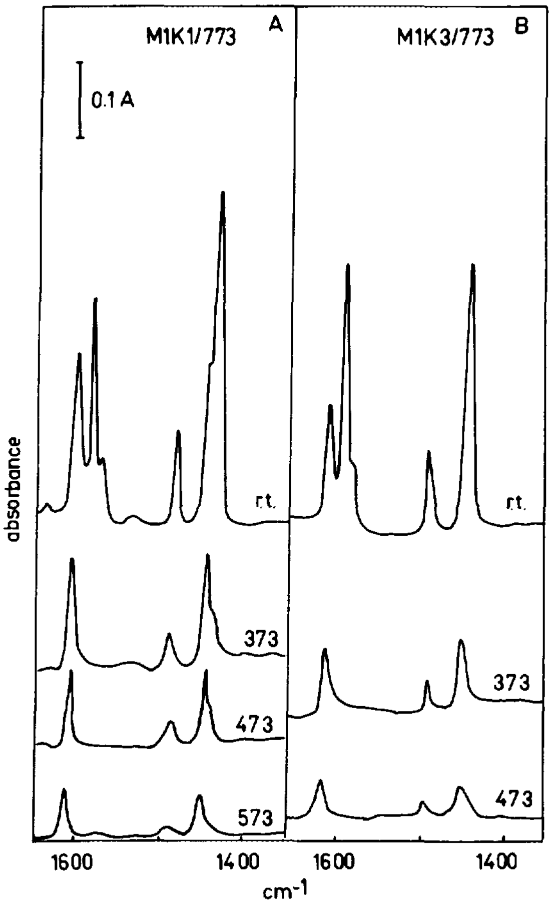

FIG. 5. FT-IR spectra recorded after adsorption of py at room temperature on samples (A) M1K1/773 and (B) M1K3/773 and outgassing at the indicated temperatures.

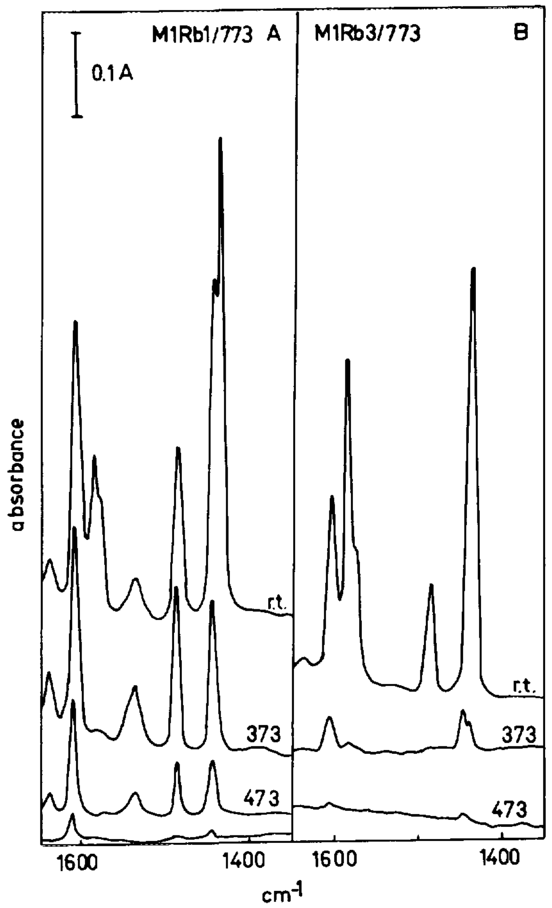

FIG. 6. FT-IR spectra recorded after adsorption of py at room temperature on samples (A) M1Rb1/773 and (B) M1Rb3/773 and outgassing at the indicated temperatures.

due to adsorption of py on both Lewis and Brønsted surface acid sites. As with other samples, splitting of the bands due to ν_{19b} and ν_{8a} modes of Lpy sites is also observed; in this case, bands at lower wavenumbers (associated with Rb^+ species) are stronger than those associated with Mo^{6+} species, but the former are removed at lower outgassing temperatures and those due to adsorption on Mo^{6+} sites remain up to 573 K. Also, the concentration of Brønsted sites is very much lower than that in the Alk-free samples, with a Bpy/Lpy ratio close to 0.2.

A similar behavior is observed for the Rb-rich sample (Fig. 6B). The only difference is that no band ascribable to pyridinium species is recorded; that is, the relatively high Rb concentration destroys the Brønsted sites that are created upon introduction of molybdenum onto the titania surface (cf. the results for the Alk-free samples). With regard to the stability of the bands due to adsorbed py, the results are similar to those found with other Alk-containing samples described above: bands associated with adsorption of py on Rb^+ species (1586 and 1440 cm^{-1}) are removed at temperatures lower than those corresponding to adsorption of py on Mo^{6+} sites (1605 and 1447 cm^{-1}).

Low-Loaded Lithium-Containing Samples

As mentioned above, the samples prepared differ in the nature of the alkali cation, but not in their weight content. Thus, although their weight percentage remains constant, their molar concentration decreases as we move downward through the alkali group. As a result, the differences observed in the behavior shown by the different samples could be related not only to the intrinsic differences in the polarizing power of the alkali cations, but also to (or instead of) their different molar concentrations. In order to check this point, as the main differences are found between the Li-containing samples and those containing the other alkali cations, we prepared a sample with the same Li molar content as that of K in sample M1K1. The spectrum recorded after adsorption of py for sample M1Li0.18 is shown in Fig. 7. The value calculated for the Bpy/Lpy ratio is only 0.04, very much lower than that for sample M1K1 (0.1). Moreover, bands due to adsorption on Mo^{6+} Lewis acid sites (1607 cm^{-1}) and Brønsted acid sites (1536 cm^{-1}) are hardly detected. Hence, we conclude that although the alkali concentration has an effect on the surface acidity, the nature (i.e., the polarizing ability) of the alkali cations also plays an important role.

Figure 8 shows changes in the Bpy/Lpy ratio for samples M1Alk1/773. The decrease observed is due both to an increase in the concentration of Lewis surface acid sites and to a decrease in Brønsted acid sites, although the first one seems to be more important. For the Alk-rich samples (3%), Brønsted sites are completely cancelled (Bpy/Lpy = 0).

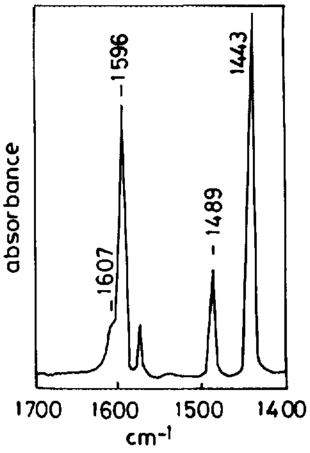

FIG. 7. FT-IR spectrum recorded after adsorption of py at room temperature on sample M1Li0.18/773 and outgassing at the same temperature.

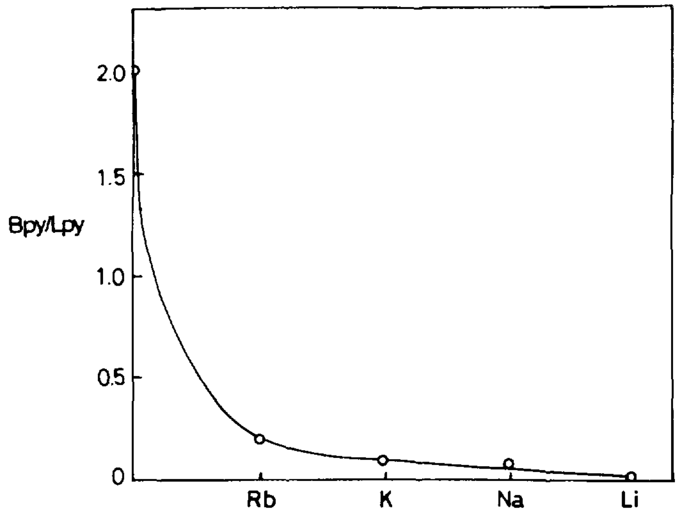

FIG. 8. Change in the Bpy/Lpy ratio with the nature of the dopant alkali cation for samples M1Alk1/773.

CONCLUSIONS

Parent titania exhibits only surface Lewis acid sites, associated with Ti^{4+} species; upon incorporation of molybdenum (Mo^{6+}), surface acidity increases significantly, with Brønsted acid sites (Mo–OH) being formed. If an alkali cation is also present, this surface acidity decreases, due to the basic character of this alkali dopant.

In addition, incorporation of the alkali species gives rise to weak Lewis acid sites (coordinatively unsaturated alkali cations). If the alkali cation is strongly polarizing (Li^+), only weak Lewis surface acid sites are detected. For less polarizing alkali cations (K^+, Rb^+), however, two types of Lewis surface acid sites are detected, even for relatively high alkali contents (3% w/w), which are associated with coordinatively unsaturated Mo^{6+} and Alk^+ species. In addition, it should be stressed that as the Alk content and/or the polarizing ability of the alkali cations is increased, a decrease in the surface concentration of Brønsted acid sites is observed, due to reaction of the alkali cations with dispersed molybdate species to form the corresponding alkali molybdates, thus destroying the Brønsted acid Mo–OH sites.

When the samples are outgassed at increasing temperatures, the intensities of all bands due to adsorbed pyridine decrease; this effect is more important for bands due to adsorption on Lewis surface acid sites than for those originating from adsorption on surface Brønsted sites. As the polarizing ability and/or concentration of the alkali dopant increases, pyridine is completely removed upon outgassing at lower temperatures, thus accounting for the presence in these samples of weak acid sites due to formation of alkali molybdates, detected by X-ray diffraction.

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